



## Short communication

## Tetramethylammonium difluoro(oxalato)borate dissolved in ethylene/propylene carbonates as electrolytes for electrochemical capacitors

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## HIGHLIGHTS

- TMADFOB dissolved in EC/PC as electrolyte for electrochemical capacitors.
- Ionic conductivity rises with the addition of ethylene carbonate.
- Ethylene carbonate suppresses the DFOB<sup>−</sup> intercalation into graphite.

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## ABSTRACT

Tetramethyl ammonium difluoro(oxalato)borate (TMADFOB) dissolved in the mixed solvents of ethylene and propylene carbonates (EC/PC) instead of neat PC have been proposed as the electrolyte solutions for electrochemical capacitors. The ionic conductivity of 1 M TMADFOB-EC/PC electrolyte solutions has been measured. It climbs up monotonously as EC content increases. Accordingly, the power density of electric double-layer capacitors is enhanced with certain EC addition. The optimum EC content for the power of EDLCs is about 30 volume percentage in the mixed EC/PC solvents. This tendency has been testified by impedance study. The electrochemical behavior of activated carbon/graphite capacitors using these electrolyte solutions has also been studied by galvanostatic charge–discharge test and the charge storage mechanism at the graphite positive electrode has been investigated by *in situ* XRD and *ex situ* Raman. The effect of EC addition on DFOB<sup>−</sup> intercalation into graphite has also been addressed at both room and elevated temperatures.

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## 1. Introduction

Accompanying the intemperate consumption of energy and resources on the earth, human society starts to care the worldwide problem of energy storage and transformation. In the past decades, there are two families of electric energy storage devices, lithium-ion batteries and electrochemical capacitors, have caught the eyes of many researchers. Both boomed in the 1990's. Soon after lithium-ion batteries outpaced electrochemical capacitors in various application fields. Then the balance between these two families got more and more tilted towards lithium-ion batteries. Once an electrode or electrolyte material was discovered or

devised, it was more likely considered to meet the needs of lithium-ion batteries instead of electrochemical capacitors.

Recently, lithium difluoro(oxalato)borate (LiDFOB) has appeared as a promising electrolyte salt in lithium-ion batteries by virtue of its hydrolytic and thermal stability, compatibility with some cathode materials and beneficial effect on the solid electrolyte interface (SEI) formation at graphite anodes, etc. [1–9]. In contrast, electrolyte salts based on DFOB<sup>−</sup> anion have received much less attention in the community of electrochemical capacitors. In order to enhance the storage ability of the porous carbon negative electrode in an non-aqueous electric double-layer capacitor, Sasaki et al. first proposed tetramethyl ammonium difluoro(oxalato)borate (TMADFOB) as the electrolyte salt because of its high solubility in propylene carbonate (PC) and the small cation size [10]. Afterward, we utilized TMADFOB in the asymmetric capacitor of activated carbon/graphite [11]. The practical application of this electrolyte salt,

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however, is problematic because of the low ionic conductivity of TMADFOB dissolved in PC, even inferior to most electrolyte solutions commercialized today (say, 1 M tetraethyl ammonium tetrafluoroborate (TEABF<sub>4</sub>) dissolved in PC, 13 mS cm<sup>-1</sup>). This shortcoming may decrease the power density of an electrochemical capacitor. Therefore, we attempted to enhance the ionic conductivity of TMADFOB solutions by using ethylene carbonate (EC) as a co-solvent mainly due to its high dielectric constant. Moreover, the molecular structures of EC and PC are very near, only differing by one methyl group. So both the solvents are quite miscible because like dissolves like.

Since solvents can considerably influence the properties of an electrode/electrolyte interface, EC addition into TMADFOB-based electrolyte solutions may play an important role in determining the behavior of electrochemical capacitors. In this study, we applied the electrolyte solutions of TMADFOB-EC/PC in both the symmetrical AC/AC and asymmetric AC/graphite capacitors. The electrochemical performance of both types of capacitors was tested and its dependency upon the EC content in the binary mixed solvents was investigated.

## 2. Experimental

### 2.1. Preparation of TMADFOB salt

The TMADFOB salt was synthesized according to the procedure introduced in the reference [12] and confirmed by H NMR (hydrogen nuclear magnetic resonance) and ITMS (ion trap mass spectroscopy).

### 2.2. Electrochemical measurements

The AC sample was PW15M13130 from Kureha Co. Ltd. and its physical properties have been described in a previous report [13]. The graphite sample was natural graphite flakes purified by Kansai Coke and Chemicals Co. Ltd. Their morphological features are shown in Fig. 1. In a capacitor (coin cell), the weight ratio of negative to positive electrode materials was kept at 1. Main electrolyte solutions were 1 M TMADFOB dissolved in the mixed solvents of EC and PC. 1 M TEABF<sub>4</sub>-PC and TEAPF<sub>6</sub>-EC/PC were also employed for comparison. The coin cell fabrication and glove box conditions were similar to those described in the past reports [13,14]. Unless otherwise specified, the galvanostatic charge-discharge tests of the coin cells were performed at the constant current density of 0.4 mA cm<sup>-2</sup>. The cut-off voltages were 0 and 2.7 V for the EDLCs with two symmetrical AC electrodes. In the case of asymmetric capacitors, the cut-off voltages were set at 0 and 3.5 V. Charge storage ability of the total capacitor (coin cell) was expressed in the terms of capacity (mAh g<sup>-1</sup>). The capacity values

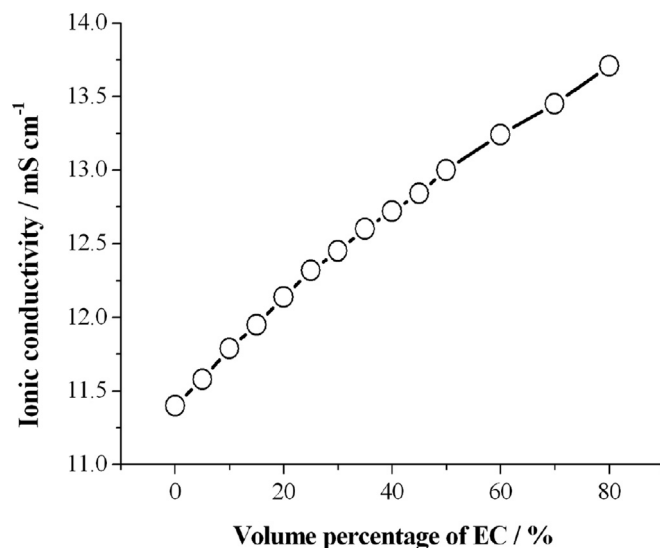


Fig. 2. Relationship between the ionic conductivity of a 1 M TMADFOB-EC/PC electrolyte solution and the EC content in the mixed solvents.

were calculated according to the following formula:  $Q = IT/w_+$  ( $I$ , the constant current (mA);  $T$ , the time for charge or discharge between cut-off voltages (hour);  $w_+$ , the weight of the positive electrode material (gram)).

The details of *in situ* XRD measurements on the graphite positive electrode in an asymmetric AC/graphite capacitor were described in the reference [13]. The Al foil was used as both the current collector and X-ray window.

## 3. Results and discussion

In the electrolyte solutions using neat PC solvent, the conductivity reaches the maximum value at the concentration of 1.6 M [10]. At lower concentrations, the conductivity strongly relies on the number of free ions, rather than the mobility of ions in the electrolyte solutions [15]. Fig. 2 depicts the relationship between the ionic conductivity of the 1 M TMADFOB solution and the EC content in the mixed solvents. The conductivity value monotonously rises up as the EC content increases. This clear trend can be interpreted as follows. Along with the addition of EC, the dielectric constant of the binary solvent apparently gets higher, and then helps enlarge the number of free ions. On the other hand, EC has a slightly higher viscosity than PC, which may somehow retard the motion of ions in the electrolyte solutions. But this influence can be neglected at the concentration of 1 M. As a result, these two conflicting factors contribute to the monotonous increase in conductivity with the EC addition. It should

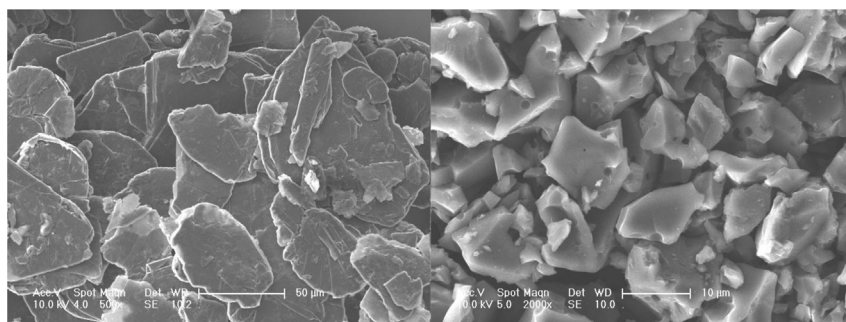


Fig. 1. SEM images of natural graphite flakes (left side) and activated carbon (right side).

be noted that as the volume content of EC in the binary solvent exceeds 50%, the conductivity values of 1 M TMADFOB-EC/PC solutions become higher than  $13 \text{ mS cm}^{-1}$  (corresponding to 1 M TEABF<sub>4</sub>-PC). This fact makes some promise for the practical applications of 1 M TMADFOB-EC/PC solutions in some electrochemical capacitors.

Fig. 3 compares the Ragone plots of EDLCs (AC/AC capacitors) using 1 M TMADFOB-EC/PC electrolyte solutions. With smaller amounts of EC addition into the electrolyte solution of TMADFOB-PC, the power density of an EDLC becomes improved, even exceeds that corresponding to 1 M TEABF<sub>4</sub>-PC. However, the relationship between the power density and the EC content as depicted in Fig. 4 doesn't follow the monotonous climb-up trend of electrolytic conductivity in Fig. 2. Given a current density, the power density value delivered by an EDLC at first rises up before reaching a maximum at the EC volume content of 30%, then it starts to drop down as EC gets dense in the binary solvents mixture. The above fact may imply that ionic motion in the bulk electrolyte solutions is not the principle step determining the kinetic traits of an EDLC. The other consecutive processes, like the transport of ions from the bulk electrolyte solution into the pores of an AC electrode (including desolvation of ions), and diffusion inside these pores, may also play very important roles. At present we can't differentiate these factors clearly by experimental means.

On the other hand, the power trait of an EDLC can be unambiguously assessed by impedance spectroscopy [16]. Fig. 5 compares the impedance results of EDLCs using different electrolyte solutions. In their Nyquist plots (Fig. 5(a)), there is little difference in the resistance values of EDLCs in the high frequency range. This fact can be easily understood since the changes of electrolytes conductivity are not big enough. At lower frequencies, pure capacitance characteristics are exhibited. A large shift of the real-part resistance can be seen in the medium frequency range, which involves the ion movements within electrode structure and across the electrode/electrolyte interface. Fig. 5(b) exhibits the relationship between  $C''$  vs. frequency. The imaginary part of the capacitance ( $C''$ ) goes through a maximum at a frequency  $f_0$ , defining a time constant as  $\tau = 1/2\pi f_0$ , which can evaluate the power performance of an EDLC. Time constants for the four electrolyte solutions are 5.34 s for 1 M TEABF<sub>4</sub>-PC, 7.19 s for 1 M TMADFOB-PC, 5.34 s for 1 M TMADFOB-EC:PC(3:7), and 9.71 s for 1 M TMADFOB-EC:PC(1:1), respectively. Thus the order of these time constants agrees with the rank in power performance as demonstrated in Fig. 4. Furthermore, Fig. 5(c) gives normalized imaginary part  $|Q|/|S|$  and real part  $|P|/|S|$  of the complex power vs. frequency. All these EDLCs behave like a pure capacitor at low

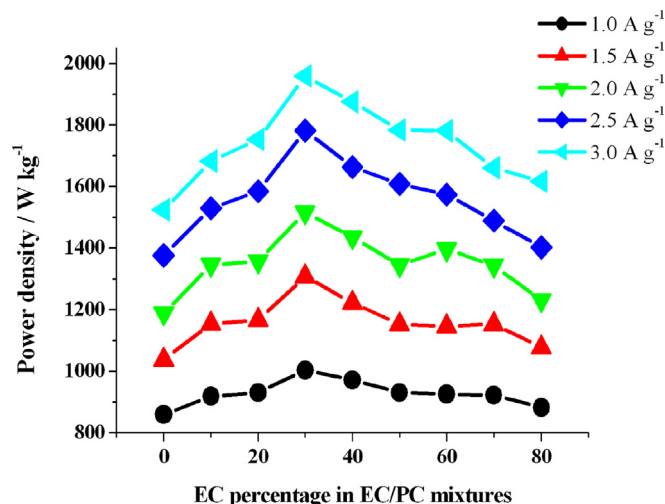


Fig. 4. Relationship between the power density of an EDLC under the charge-discharge test at different current densities and the EC content in the mixed solvents of 1 M TMADFOB-EC/PC electrolyte solutions.

frequencies and a resistance at high frequencies. However, the EDLC using the electrolyte solution of 1 M TMADFOB-EC:PC(3:7) demonstrates the most prominent climb-up pace in  $|Q|/|S|$  as the frequency falls down, which proves its satisfactory power performance.

Fig. 6 exhibits the cycle performance of EDLCs using different electrolyte solutions. The presence of EC contributes almost no detrimental influence on the cycle ability of an EDLC.

On the contrary, the applications of 1 M TMADFOB-EC/PC solutions in AC/graphite capacitors are not optimistic. Fig. 7 compares the initial discharge capacity values of AC/AC and AC/graphite capacitors using 1 M TMADFOB-EC/PC solutions. The influence of EC content on the discharge capacity of AC/AC capacitor is almost unperceivable. These capacity values fluctuate around about  $35 \text{ mAh g}^{-1}$ . In contrast, in the cases of AC/graphite capacitors, the discharge capacity decreases with the increase of EC content in the electrolyte solutions. Especially, the drop-down tendency becomes more drastic in the EC volume percentage range from 15% to 40%. Similar phenomenon was discovered in the case of AC/graphite capacitors using the electrolyte solutions of SBPPF<sub>6</sub>-EC/PC (SBP stands for spiro-(1,1')-bipyrrolidinium) [17]. This capacity fading along with the EC addition was attributed to the strong solvation of the anions by EC molecules, which may prevent the anions from intercalating into graphite positive electrodes. Theoretical calculations have predicted some preferential interaction between EC and the anions like BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> [18–20]. The estimated binding energy differences between EC and PC molecules towards the same anion are in the order of magnitude of several  $\text{KJ mol}^{-1}$ . In this study, the EC volume percentage of 40% in the binary solvent is a critical point where the capacity declining starts to level off. At this point nearly all the DFOB<sup>-</sup> anions in the electrolyte solutions can be considered as being tightly bond to EC molecules and the intercalation of DFOB<sup>-</sup> into graphite positive electrode is effectively suppressed. Here the molar ratios of EC and PC solvent molecules to DFOB<sup>-</sup> anion equal to about 6 and 7, respectively ( $[\text{EC}]/[\text{DFOB}^-] = (40 \times 1.32/88.6)/(1 \times 100/1000) = 5.96$ ;  $[\text{PC}]/[\text{DFOB}^-] = (60 \times 1.20/102.1)/(1 \times 100/1000) = 7.05$ , the details of calculation was introduced in the reference [17]). This value of  $[\text{EC}]/[\text{DFOB}^-]$  is much larger than that of  $[\text{EC}]/[\text{PF}_6^-]$  (near 1), which hints that the linkage between DFOB<sup>-</sup> and EC is not so intense as that between PF<sub>6</sub><sup>-</sup> and EC. Furthermore, the solvation of DFOB<sup>-</sup> by EC appears just a little prior to that by PC molecules. This big contrast

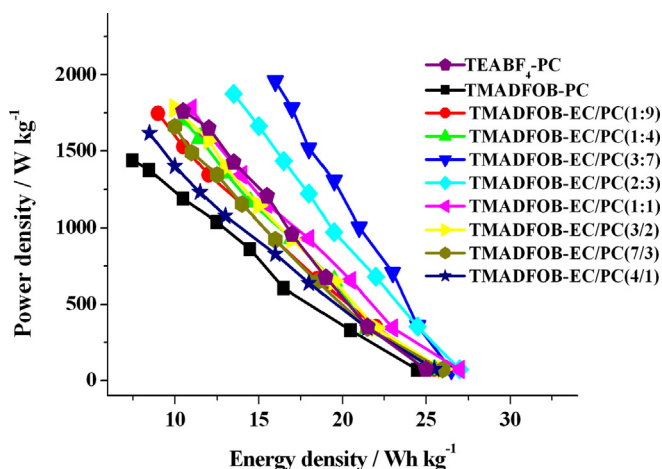


Fig. 3. Ragone plots of EDLCs (AC/AC capacitors) using 1 M electrolyte solutions.

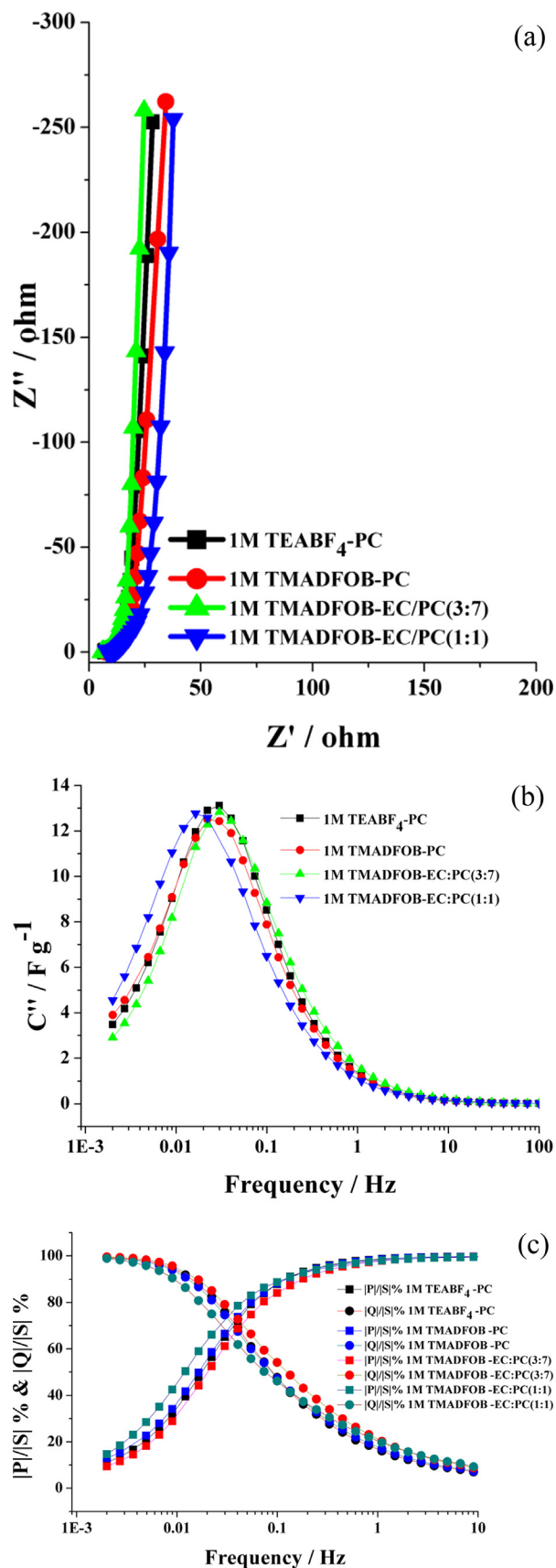


Fig. 5. Impedance results of the EDLCs using different electrolyte solutions, (a) Nyquist plots; (b) relationship between  $C''$  and frequency; and (c) normalized reactive power  $|Q|/|S|$  and  $|P|/|S|$  vs. frequency.

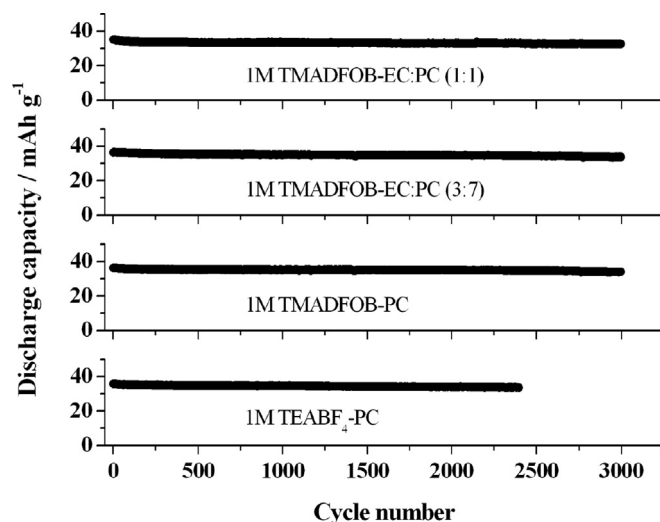


Fig. 6. Cycle performance of EDLCs using different electrolyte solutions.

between DFOB and PF<sub>6</sub> may be attributed not only to their different sizes (the van der Waals volumes: DFOB<sup>-</sup>, 77 Å<sup>3</sup>; PF<sub>6</sub><sup>-</sup>, 69 Å<sup>3</sup>) [11,21], but also to their unlikeness in geometric symmetry.

To verify the blocking effect of EC addition on DFOB<sup>-</sup> intercalation into graphite positive electrode, *in situ* XRD measurements were conducted on AC/graphite capacitors. Fig. 8(a) shows the *in situ* XRD patterns of the graphite positive electrode in the AC/graphite capacitor using the electrolyte of 1 M TMADFOB dissolved in PC. With the rise in the cell voltage of the AC/graphite capacitor, the (002) peak of graphite (26.5°) becomes weaker and new diffraction peaks emerge. The most prominent new peak locates at a lower diffraction angle close to 26.5°. The splitting of the graphite (002) peak starts at the cell voltage of 2.3 V, which is a sign of DFOB<sup>-</sup> intercalation into the interlayer galleries between the adjacent graphene layers of the graphite positive electrode. In an analogous study using KS6 as the positive electrode, DFOB<sup>-</sup> intercalation occurs at a cell voltage over 3.7 V. There are some disorders and defects in KS6 that can obstruct from ions intercalation [14].

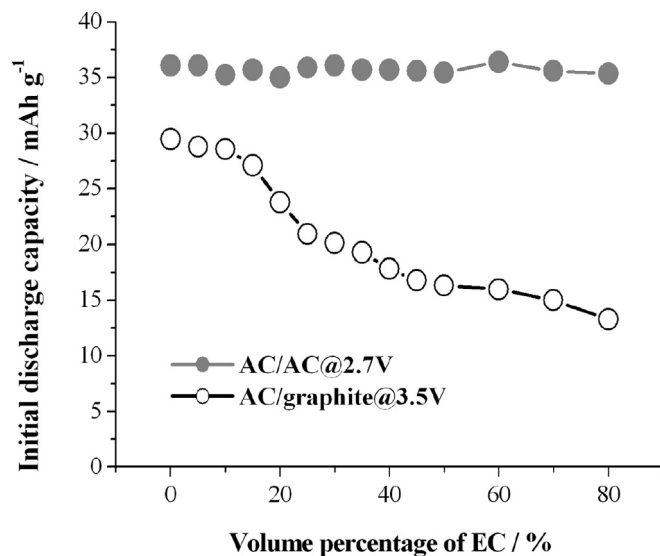


Fig. 7. Relationship between the initial discharge capacity of an EDLC or AC/graphite capacitor and the EC content in the mixed solvents of 1 M TMADFOB-EC/PC electrolyte solutions.



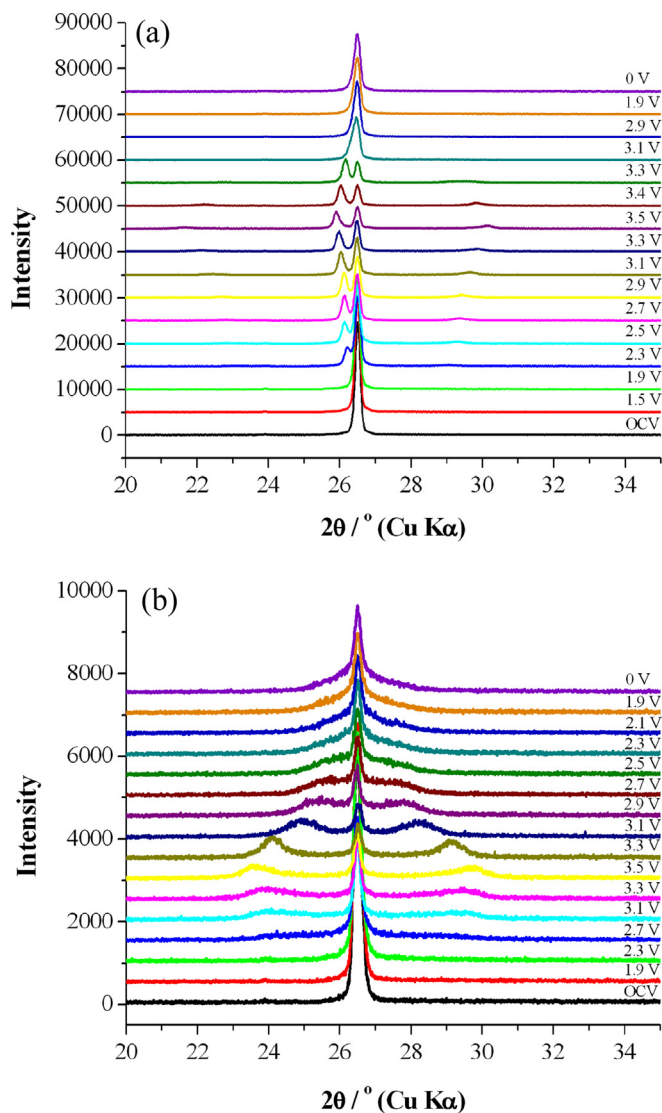


Fig. 8. *in situ* XRD patterns of the graphite positive electrode in the AC/graphite capacitor using the electrolyte of 1 M TMADFOB dissolved in PC (a) or EC/PC (volume ratio 1 to1) (b), respectively.

The positive electrode material utilized in this study was natural graphite flakes, which is highly crystalline. This may be the main reason for the fluent intercalation of DFOB<sup>−</sup> at lower cell voltages. In contrast, after adequate addition of EC, the intercalation of anions into graphite lags behind. Fig. 8(b) demonstrates the *in situ* XRD patterns of the graphite positive electrode in the AC/graphite capacitor using the electrolyte of 1 M TMADFOB dissolved in the mixed solvents of EC and PC (EC and PC have the same volume). Here the intercalation of DFOB<sup>−</sup> into natural graphite begins at 3.1 V. Besides the (002) peak of graphite, there are two new diffraction peaks residing at both sides of it. As the cell voltage rises, the left side peak shifts to a lower while the right-side peak migrates to a higher diffraction angle, and the interval between these two peaks becomes widened. In the case of PF<sub>6</sub><sup>−</sup>, the (002) peak of graphite keeps almost intact and no intercalation happens after more than 10% EC addition by volume at the cell voltages over 4 V [17]. As discussed from Fig. 7, the binding between DFOB<sup>−</sup> and EC is much milder than that between PF<sub>6</sub><sup>−</sup> and EC, and even seems comparable to that between DFOB<sup>−</sup> and PC. Although the addition of EC can decrease the capacity of AC/graphite remarkably as

Table 1

Parameters of the GICs (graphite intercalation compounds) at 3.5 V in Fig. 8.

Electrolyte solution	Basal repeat length along C/Å	Stage no.	Intercalated gallery height/Å
1 M TMADFOB-PC	21.68	5	8.26
1 M TMADFOB-EC/PC	14.91	3	8.20

illustrated in Fig. 7, the intercalation of DFOB<sup>−</sup> into graphite can still be detected in the *in situ* XRD measurements. Anyhow, the intercalation of DFOB<sup>−</sup> into natural graphite in the presence of EC is not easy. The diffraction peaks of graphite intercalation compounds (GIC) in Fig. 8(b) are much broader than those in Fig. 8(a), which means the smaller crystallite size of GIC formed in the presence of EC. If we adopted the calculation method introduced in the previous studies [22,23], and took the two strongest peaks of GIC (except for graphite (002) peak at 26.5°) at 3.5 V in Fig. 8(a) and (b) as the (n + 2) and (n + 1) diffraction peaks for the Stage-n GIC, respectively, we could obtain the key parameters of GICs in the AC/graphite capacitors at 3.5 V, as listed in Table 1. The intercalated gallery heights of GICs using the electrolyte solutions with and without EC are essentially indistinguishable. Therefore, it is hard to deduce that EC co-intercalates with DFOB<sup>−</sup> into graphite at the present stage. Rather, it is likely that some EC molecules may be stripped off from DFOB<sup>−</sup> before the anion intercalation into graphite. In the previous study [17], we have shown that EC co-intercalates with BF<sub>4</sub><sup>−</sup> into graphite. Accordingly, the affinity between the anions and EC molecules ranks as BF<sub>4</sub><sup>−</sup>-EC > PF<sub>6</sub><sup>−</sup>-EC > DFOB<sup>−</sup>-EC.

Besides XRD characterizations, Raman microcopy is also a powerful tool to probe graphite intercalation compounds [24,25]. We measured *ex situ* Raman spectra (Fig. 9) of graphite positive electrodes recovered from the AC/graphite capacitors charged to 3.5 V. The G band (1578 cm<sup>−1</sup>) of graphite splits into a doublet peak (E2g2 (i) at 1578 cm<sup>−1</sup> and E2g2 (b) at 1600 cm<sup>−1</sup>) for both the electrolytes of 1 M TMADFOB dissolved in pure PC and the mixed EC/PC solvents. This means that anions intercalate into graphite positive electrode in both cases. In the Raman spectrum corresponding to the electrolyte of TMADFOB dissolved in neat PC, the E2g2 (b) band are apparently stronger than the E2g2 (i) band. On the contrary, the Raman spectrum corresponding to the electrolyte of TMADFOB dissolved in the mixed solvent EC/PC gives an opposite result. Since the intensity ratio of E2g2 (i) to E2g2 (b) band is

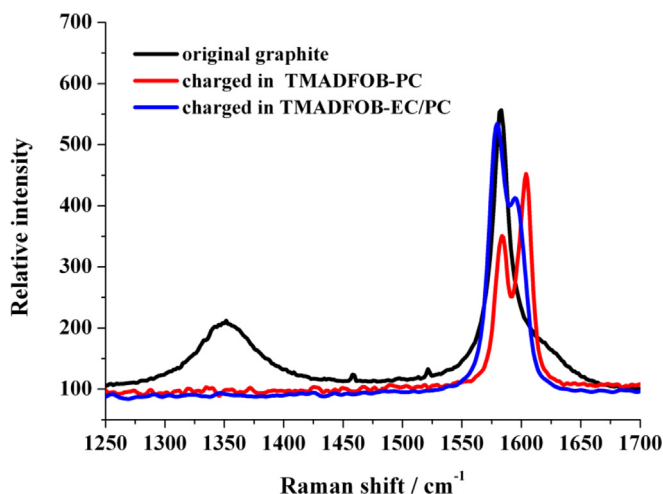


Fig. 9. *ex situ* Raman spectra of graphite positive electrodes recovered from AC/graphite capacitors charged to 3.5 V.

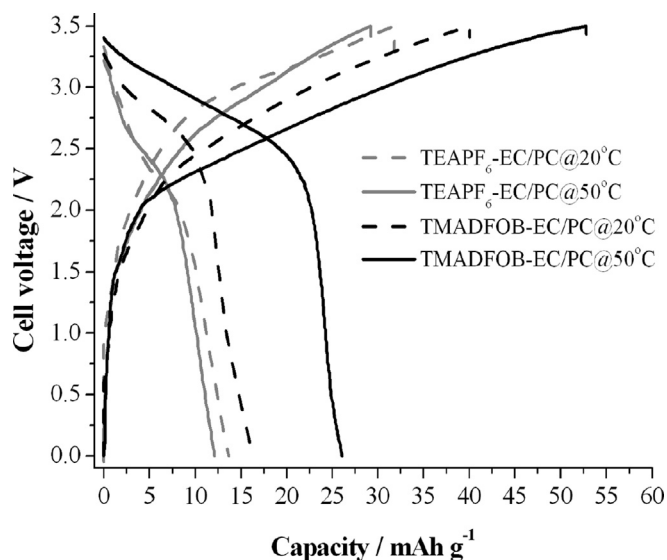


Fig. 10. Initial galvanostatic charge-discharge curves of AC/graphite capacitors using the electrolyte solutions of 1 M TMADFOB or TEAPF<sub>6</sub> dissolved EC/PC (volume ratio 1 to 1), at room temperature and 50 °C, respectively.

proportional to the stage number, we can deduce that the graphite-anion intercalation compound obtained in the presence of sole PC solvent has a lower stage number. However, this deduction is in conflict with the stage numbers in Table 1. It should be emphasized here that *ex situ* Raman spectra can't provide accurate information on the structures of graphite positive electrodes under the same environments as in AC/graphite capacitors. For instance, we have monitored the open circuit voltages (OCVs) after charging AC/graphite capacitors to 3.5 V. The OCV of the capacitor using pure PC solvent fades down much more slowly than that using the EC/PC mixed solvents. The graphite electrode recycled from the latter capacitor already deviate from the charge state at 3.5 V far away when subjected to *ex situ* Raman measurements. Therefore, *in situ* Raman study on these electrode/electrolyte systems is urgent.

A complimentary experiment can further evince that the binding strength of PF<sub>6</sub><sup>-</sup>-EC is larger than that of DFOB<sup>-</sup>-EC. Fig. 10 demonstrates the initial galvanostatic charge-discharge curves of AC/graphite capacitors using the 1 M electrolyte solutions of EC/PC mixture (1–1 by volume) at 20 °C and 50 °C, respectively. In the case of 1 M TEAPF<sub>6</sub> dissolved in EC/PC, the discharge capacity values delivered by the AC/graphite capacitors were quite low at both the room and elevated temperatures, which means that the firm interaction between PF<sub>6</sub><sup>-</sup> and EC sufficiently retards the anion intercalation into graphite. On the contrary, for the electrolyte solutions of 1 M TMADFOB dissolved in EC/PC, the discharge capacity increases considerably with the rise in temperature, which is a sign of the release of “free” anions from the shackle of EC binding and the facile anion intercalation into the graphite positive electrode. The above phenomenon may hint that the specific “attraction” between DFOB<sup>-</sup> and EC is too loose to withstand the thermal disturbance.

#### 4. Conclusion

So far, we have shown that EC addition into the electrolyte solution of TMADFOB-PC can increase its ionic conductivity gradually. Moreover, the electrolyte solutions of TMADFOB-EC/PC have some potential applications in practical EDLCs in terms of enhanced power density. On the contrary, for the AC/graphite capacitor, EC addition retards DFOB<sup>-</sup> intercalation into graphite positive electrodes, and thus decreases the reversible capacity of the capacitor. *in situ* XRD results of graphite positive electrodes demonstrates that the anion intercalation takes place even with higher EC contents, but at higher cell voltages. The expansion extent of the interlayer space in graphite electrode due to DFOB<sup>-</sup> intercalation bears little relationship with the presence of EC in an electrolyte solution. The suppression effect of EC on DFOB<sup>-</sup> intercalation into graphite can be lessened at elevated temperatures, which may indicates the weak affinity between DFOB<sup>-</sup> and EC.

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#### References

- [1] S.S. Zhang, *Electrochem. Commun.* 8 (2006) 1423–1428.
- [2] S.S. Zhang, *J. Power Sources* 163 (2007) 713.
- [3] Z. Chen, Y. Qin, J. Liu, K. Amine, *Electrochem. Solid-State Lett.* 12 (2009) A69.
- [4] M.H. Fu, K. Huang, S.Q. Liu, J.S. Liu, Y.K. Li, *J. Power Sources* 195 (2010) 862.
- [5] S.S. Zhang, *ECS Trans.* 3 (2007) 59.
- [6] Z. Zhang, X. Chen, F. Li, Y. Lai, J. Li, P. Liu, X.J. Wang, *J. Power Sources* 195 (2010) 7397.
- [7] J. Liu, Z. Chen, S. Busking, K. Amine, *Electrochem. Commun.* 9 (2007) 475.
- [8] S.-H. Kang, D.P. Abraham, A. Xiao, B.L. Lucht, *J. Power Sources* 175 (2008) 526.
- [9] J. Liu, Z. Chen, S. Busking, I. Belharouak, K. Amine, *J. Power Sources* 174 (2007) 852.
- [10] N. Nanbu, K. Suzuki, T. Ebina, H. Uno, Y. Sasaki, *Electrochemistry* 75 (2007) 615.
- [11] Y. Wang, C. Zheng, L. Qi, M. Yoshio, K. Yoshizuka, H. Wang, *J. Power Sources* 196 (2008) 10507.
- [12] T. Herzig, C. Schreiner, D. Gerhard, P. Wasserscheid, H.J. Gores, *J. Fluor. Chem.* 128 (2007) 612.
- [13] H. Wang, M. Yoshio, A.K. Thapa, H. Nakamura, *J. Power Sources* 169 (2007) 375.
- [14] H. Wang, M. Yoshio, *Electrochem. Commun.* 8 (2006) 1481.
- [15] H.P. Chen, J.W. Fergus, B.Z. Zhang, *J. Electrochem. Soc.* 147 (2000) 399.
- [16] P.L. Taberna, P. Simon, J.F. Fauvarque, *J. Electrochem. Soc.* 150 (2003) A292.
- [17] H. Wang, M. Yoshio, *Chem. Commun.* 46 (2010) 1544.
- [18] L. Xing, W. Li, C. Wang, F. Gu, M. Xu, C. Tan, J. Yi, *J. Phys. Chem. B* 113 (2009) 16596.
- [19] T. Li, P.B. Balbuena, *J. Electrochem. Soc.* 146 (1999) 3613.
- [20] E. Endo, M. Ata, K. Tanaka, K. Sekai, *J. Electrochem. Soc.* 145 (1998) 3757.
- [21] M. Ue, A. Murakami, S. Nakamura, *J. Electrochem. Soc.* 149 (2002) A1385.
- [22] X. Zhang, N. Sukpirom, M.M. Lerner, *Mater. Res. Bull.* 34 (1999) 363.
- [23] P.W. Ruch, M. Hahn, F. Rosciano, M. Holzapfel, H. Kaiser, W. Scheifele, B. Schmitt, P. Novák, Kötzt, A. Wokaun, *Electrochim. Acta* 53 (2007) 1074.
- [24] L.J. Hardwick, M. Hahn, P. Ruch, M. Holzapfel, W. Scheifele, H. Buqa, F. Krumeich, P. Novák, R. Kötzt, *Electrochim. Acta* 52 (2006) 675.
- [25] M. Inaba, H. Yoshida, Z. Ogumi, T. Abe, Y. Mizutani, M. Asano, *J. Electrochem. Soc.* 142 (1995) 20.